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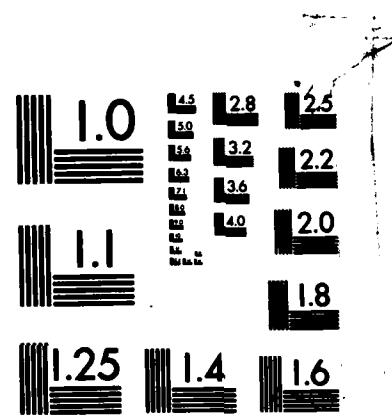
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High Temperature Oxide Electrolytes for the
Splitting of Water -- The ROC Process

by

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and
Jon E. Noring

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HIGH TEMPERATURE OXIDE ELECTROLYTES FOR THE SPLITTING OF WATER-- THE ROC PROCESS

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ABSTRACT

Solid oxygen passing membranes such as stabilized zirconia have been proposed for use as membranes in high temperature water splitting processes. This paper describes two-membrane systems, ROCs, which use a hydrogen passing membrane as well. An advantage of a two-membrane system is that water may be split in a single passage through the device, thus decreasing substantially thermodynamic losses associated with the heat exchanger and other appurtenances. Some problems such as the stability of hydrogen passing membranes in a water atmosphere are addressed. It is suggested that the ROC process may provide a means of protecting hydrogen passing membranes, and that electric ROCs may be unusually well suited for operation at temperatures at which palladium membranes might be used. The thermal efficiencies of two membrane systems with and without electrical enhancement are compared.

I. INTRODUCTION

For several years a small group at the University of Minnesota has been examining the feasibility of producing hydrogen and oxygen from water.¹⁻⁸ Our primary interest has been in using sunlight to effect the separation in a one-step process. Although we have recently completed construction of a small solar furnace and have begun to conduct experimental studies, most of our work has been analytical. It has been aimed at the evaluation of various techniques for effecting the separation. One aspect of our studies has emphasized the sources of thermodynamic losses in archetypal systems. Such losses result from entropy production in the components of devices for producing hydrogen and oxygen from water.

Our first generation devices embodied reactor-separators using effusional membranes which achieved a partial separation of

the desired products. They require the recirculation of a great deal of water. The most wasteful components of such devices, from a thermodynamic standpoint, are almost always the heat exchangers; heat exchanger losses are roughly proportional to the amount of working fluid which must be circulated through the device to produce a given amount of product. We thus sought next to minimize the amount of working fluid which must be circulated.

Our second generation of analytical devices was an imaginative extension of an idea which had been suggested earlier^{10,11}. It made use of a two-membrane reactor-separator, the ROC,⁵ which achieves a complete separation in a single pass of the water and thus requires no recirculation of working fluid. It thus achieves a substantial improvement in process efficiency by reducing irreversibilities associated with heat exchanger losses.

In the meantime, other investigators have evaluated one membrane systems which effect the separation by removing one of the components, oxygen, from the high-temperature equilibrium mixture by means of diffusion of the oxygen, under the influence of a pressure gradient or an emf.¹²⁻¹⁶ It is anticipated that such systems will entail substantial recirculation and will thus have concomitant heat exchanger losses.

In this paper, we presume that, because heat exchangers are, apparently, the most thermodynamically wasteful components of separation devices, two membrane devices, which require no recirculation, if they can be made to work, will be most worthy of further consideration. We therefore examine and compare the conventional ROC with one which makes use of a solid high temperature electrolyte and diffusion under the influence of an emf, an Electric-ROC. We also consider the possibility of electrolysis at both electrodes.

II. ONE-MEMBRANE DEVICES

Fally's¹⁶ patent, figure 1, describes the prototype one-membrane device. Several of the later devices^{10,12-15} differ from Fally's in that they propose to use an electromotive force to facilitate or effect transport of oxygen through the membrane rather than pressure alone; they are thus sometimes referred to as electrolysis cells. Although Fally claims that his device will effect virtually 100% separation, in fact, the accumulation of hydrogen on the high-pressure side of the oxygen-passing membrane and the concomitant reduction of the oxygen pressure, at a given

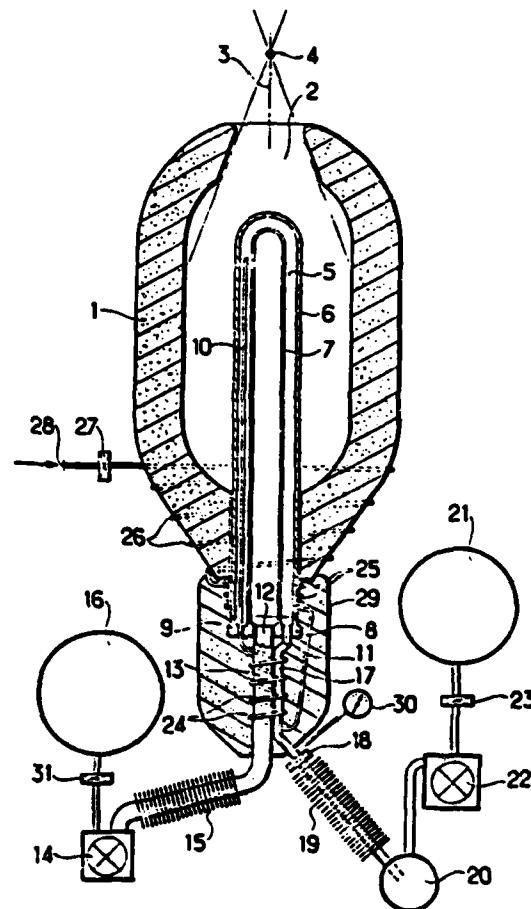


Figure 1. Fally's hydrogen generating device. (U.S. Patent 4120663, October 17, 1978) "Concentric inner tubes define an outer steam vessel with the inner tube constituted by a selective membrane consisting of a metallic oxide having a first doping to effect passage of oxygen ions through the membrane to the interior of the inner tube acting as an oxygen collector and having a second doping to effect return conduction of electrons through said membrane to increase heating of the stream. A vacuum pump is applied to the interior of the inner tube to provide a pressure difference to facilitate oxygen passage through the membrane."

operating pressure will make separation increasingly difficult and require the recirculation of a substantial fraction of the feedwater. It seems evident that a conscientious analysis of such a system, which should be done, will suggest that the optimum system will be one which makes use of a substantial amount of water recirculation. Although the authors of other papers which have concerned themselves with the one-membrane oxygen-separating devices have apparently not reported complete thermodynamic analyses of their systems, it is apparent that any one-membrane system will have associated with its operation heat exchanger losses which will be incurred because recirculation of some working fluid will be required.

III. TWO MEMBRANE DEVICES-- THE ROC

Ford¹⁰ and Nakamura¹¹ have suggested systems which embody two-membrane reactor-separators. In their systems, water heated to high temperatures is introduced into a chamber whose walls are equipped with two membranes, a hydrogen passing membrane and an oxygen passing membrane. Ihara¹⁷ has extended their work. Ford considered the use only of palladium and its alloys as hydrogen passing membranes. He was thus constrained to operate at low temperatures with high chamber pressures and inordinately high pressure drops across the membranes. Nakamura, who was concerned with the need to minimize pumping losses concluded that the reactor-separator would have to operate at temperatures above 3000K, a requirement that would make solar collection efficiencies very low and would virtually eliminate the possibility that other energy sources might be used or that suitable membrane materials might be found.

In addressing ourselves to this problem,^{1,2,5,6} we concluded that optimum temperatures for the operation of such systems would be much lower than those envisioned by Nakamura, and Ihara^{17,18,19} has since come to a similar conclusion. Our studies suggested that two-membrane systems might permit us to ameliorate the materials problems by reducing the oxygen activity in the reactor-separator in a way that was made possible by the unique reactor geometries and dead-endedness which two-membrane systems permit. We called our device the ROC, an acronym for reduced oxygen concentration, which we felt was appropriate because it was also the name of a "fabulous bird of Arabia so huge that it bore off elephants to feed its young",²⁰ but was duped by Sindbad the Sailor²¹ into serving him.

A schematic diagram of the ROC system, taken from reference 5 is shown in figure 2. The heat exchanger, cooler, and pumps of figure 2 are components of a complete archetypal system for producing hydrogen and oxygen from water, but the component of immediate interest is the two-membrane reactor-separator shown at the top of the figure. Water is fed to it through station 1. Hydrogen and oxygen are recovered from it through stations 2 and 3. When the system is operating in the steady state, the molar flow rates of hydrogen and oxygen must be in the ratio 2. In the absence of an electrical potential difference across the oxygen passing membrane, the flow rates of hydrogen and oxygen across their membranes will be monotonic functions of the appropriate partial pressure drops across them and proportional to the mass-

diffusional conductances of the two membranes.

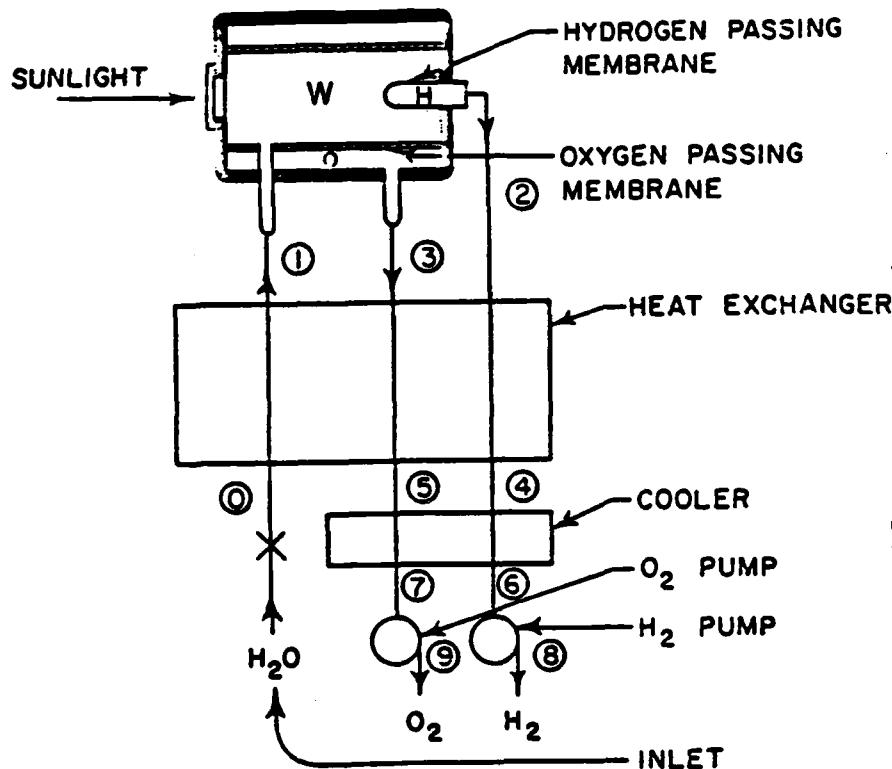


Figure 2. (from reference 5) Schematic diagram of the ROC system. Liquid water enters at atmospheric pressure and 298.15K. It is compressed (or expanded isothermally to state 0 with negligible work. The liquid water is then vaporized and brought to the temperature of the reactor-separator by heat from the descending product streams in the counter-current heat exchanger. Hydrogen and oxygen diffuse from chamber W through their respective membranes into chambers O and H. The product streams are cooled to 298.15K by passage through the heat exchanger and cooler, and are then isothermally compressed to a useful pressure, 1 atm in this case.

Inasmuch as the ratio of the flow rates must be two, the composition of the gas in chamber W will adjust itself, in accordance with the boundary conditions we impose by our choice of pressures in chambers H, O, and W, to make the ratio two. If the conductance of the hydrogen-passing membrane is made small relative to that of the oxygen-passing membrane by adjusting their dimensions, for example, the partial pressures of the gases in chamber W will adjust themselves so that the partial pressure of

hydrogen is higher and the oxygen pressure lower in chamber W than they would be at a given pressure and temperature in contact with equilibrium water. The equilibrium concentrations of the volatile oxides of the platinum group metals are therefore expected to be lower than they would be in contact with equilibrium water substance. Moreover, inasmuch as chamber W is dead-ended, there is no place for volatile oxides to go; metal membranes of iridium and perhaps even osmium might be usable in such a steady state situation.

IV. THE ELECTRIC ROC

It is pertinent to ask the question: "Would it be advantageous to combine the features of ROC reactor-separators with those of the devices which make use of electrolysis at high temperatures in solid electrolytes, to achieve water splitting?"

Superficially, it would appear that the work of electrolysis at the high reactor temperatures, to effect a separation, would be directly exchangeable for the low temperature pump work required to create the pressure drop across the oxygen-passing membrane in the ordinary ROC, and that it therefore presents us with a thermodynamically equivalent alternative. Accordingly, we have done some preliminary calculations to examine what would be the effect on the thermal efficiency of the ROC if it were to be enhanced by the use of high-temperature electrolysis, or if electrolysis were to be used in place of the pump, thus replacing it completely.

Our model is shown in figure 3. The electric ROC is very much like a conventional ROC, except that the oxygen passing membrane has been equipped with electrodes and a power supply to drive oxygen across the membrane by means of an electrical potential difference rather than a pressure difference. The low temperature mechanical pump of the conventional ROC has thus been replaced by a high-temperature electrical pump.

V. FLIGHT OF THE ROCS

In the sections which follow, we compare, for illustrative purposes, the thermodynamic performances of the devices we have described hereto. We have chosen for the comparison, a condition we have already described elsewhere.⁵ The reactor-separator

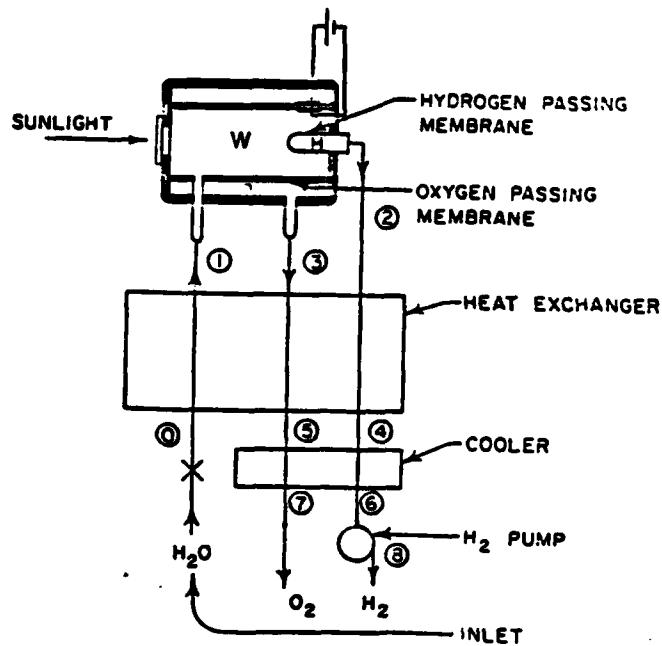


Figure 3. The electric ROC. The mechanical oxygen pump of the conventional ROC has been replaced by an electrical pump at the reactor-separator.

temperature is 2200K, the pressure is 5atm.

In the ordinary ROC, the pressure on the downstream side of the hydrogen membrane is 0.02 atm. On the downstream side of the oxygen membrane it is 0.01 atm. Both streams are pumped to ambient temperature at 298.15K.

In the electric ROC, the pressure on the downstream side of the hydrogen membrane is 0.02 atm. On the downstream side of the oxygen membrane, it is 1 atm because it has been pumped electrically.

Finally, we have introduced a third device to underscore the thermodynamic implications of our examples, the double electric ROC. Although we do not, at this time suggest any particular material with which it might be made to work, it is not difficult to imagine a cation-conducting membrane, analogous to the oxygen

conducting membrane, by means of which hydrogen might be electrically pumped, as well. Some of the beta-aluminas come to mind for this purpose.

A. The Ordinary ROC

Figures 4 and 5, taken from reference 5 show the effects of the reactor-separator temperature and pressure on the permissible downstream pressures. Each isotherm or isobar represents the boundary between the permissible (to the left) and forbidden (to the right) regions. Higher temperatures permit the pumps to operate at higher pressures because the water is more dissociated. Increasing the chamber pressure also permits the pumps to operate at higher pressures, although it decreases the extent of dissociation.

Heat flux and thermal efficiencies of our example ROC, which operates at 2200K and 5 atm, are shown in figure 6. At R, the reactor-separator operates reversibly. Point R lies on the operational boundary. At every point on the boundary the outlet gas partial pressures are just equal to those within chamber W. It is also the operating point at which the composition in W is the same as the feed composition at the entrance of the reactor-separator. Thus, there is no entropy of mixing and no entropy-producing pressure drop associated with the operation of the reactor-separator. But the limiting product production rate approaches zero as this operating point is approached. If we wish to produce hydrogen and oxygen at a reasonable rate, we must operate well to the left of the boundary.

B. Comparison of the ROCs

In the example which we use for comparison with the electric and double electric ROCs, we have chosen the operating point which lies at $P_{H_2} = 0.02$ atm, $P_{O_2} = 0.01$ atm. We have adjusted the mass conductances of the membranes so that the composition of the chamber gases in all of the ROCs are the same: $P_H = 0.00131$; $P_{H_2} = 0.05429$; $P_{H_2O} = 4.91097$; $P_{OH} = 0.01709$; $P_O = 0.00028$; and $P_{O_2} = 0.010688$. The results of our comparison are given in Table 1.

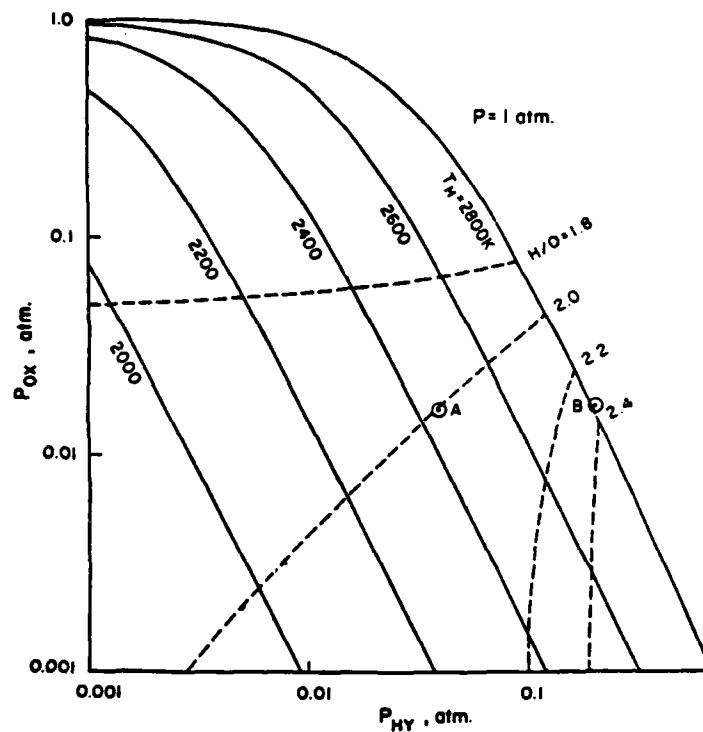


Figure 4. (from reference 5) Map, on P_{HY} - P_{OX} coordinates, which shows the variation of the locus of the operating boundary with reactor-separator temperature, at 1 atm. At each reactor-separator temperature, operation is possible at downstream pressure points which lie to the left of the appropriate isotherm. With a given set of membranes, the gas permeation rates are large far from the isotherm and approach zero as the operating point approaches the boundary. Also shown (dashed lines) are lines of constant hydrogen/oxygen ratio in chamber W. In the operation of the double electric ROC, the minimum amount of electrical work required to produce hydrogen and oxygen at one atmosphere pressure from the decomposition of one mole of water would be given by $-RT\ln(P_{H_2}P_{O_2}^{0.5})$. The amount of electrical work required to pump the oxygen alone in the electric ROC would be given by $0.5RT\ln P_{O_2}$. The remainder of the work would have to be supplied by a mechanical pump operating at ambient temperature.

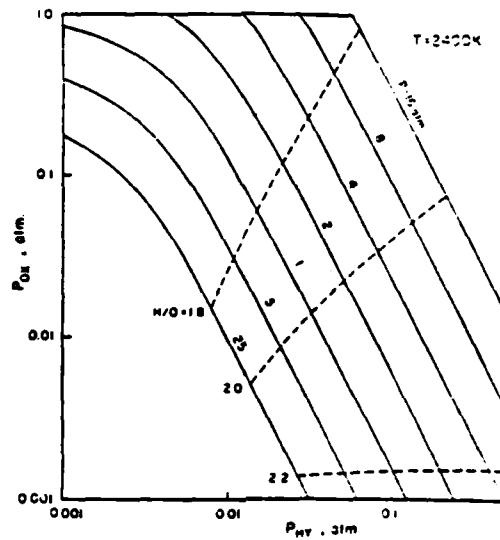


Figure 5. (from reference 5) Map, on P_{HY} - P_{OX} coordinates which shows the variation of the locus of the operating boundary position with inlet-pressure at 2400K. At each inlet pressure, operation is possible at points which lie to the left of the appropriate isobars. Lines of constant hydrogen/oxygen ratio in chamber W at the operating condition are also shown.

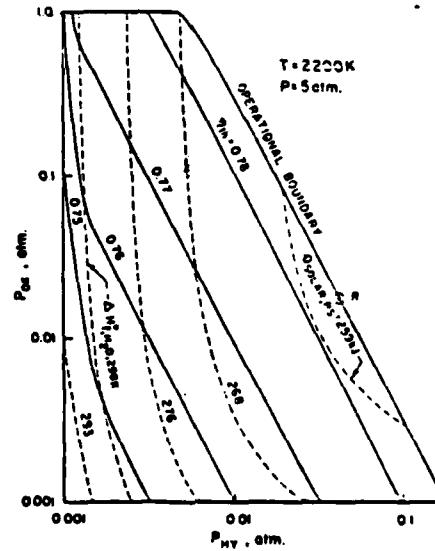


Figure 6. (from reference 5) Map, on P_{HY} - P_{OX} coordinates which shows heat-flux to the reactor-separator and thermal efficiency of the ROC. Feed pressure is 5 atm. Temperature is 2200K. State points which lie to the right of the $Q_{solar,R-S}$ line 285.84 kJ require additional heat input into the feed stream; those to the left do not.

Table 1. Performance of the ROC configurations

	ROC	EROC	DERO
heat flux to reactor, kW	285.84	243.71	172.13
pump work, kW	15.41	9.70 ^a	
electrical work, kW		42.13 ^b	113.71
thermal efficiency ^c	0.776	0.761	0.717
thermal efficiency ^d	0.731	0.635	0.520

a. hydrogen pump only; b. oxygen pump only;
 c. defined as the net work equivalent of one mole of hydrogen minus the pump and electrical work required to achieve it, divided by the heat to the reactor-separator; d. defined as the work equivalent of one mole of hydrogen divided by the heat input required by the reactor-separator plus that required to produce the electric power required for electrolysis and the pumps with an efficiency of 0.4.

Table 1 shows that the semi-idealized ROC is superior to its semi-idealized electrolysis modifications. The reason for the slight differences in the first efficiencies shown in table 1 arise from the substitution of the thermodynamically more valuable electrical work for heat in the reactor-separator. The much greater differences shown in the second efficiency reflect the likelihood that electric power may ultimately have to be furnished by a heat engine, whose efficiency here has been taken, arbitrarily, to be 0.4. But a much greater difference between one- and two-membrane systems is apt to arise in the least efficient component of a practical system, the heat exchanger. The ROCs recirculate essentially no water. They require a minimum of heat exchange.

C. ROC Variations

The electric ROC will apparently operate with lower overall efficiencies than the ROC, but it may offer one potential advan-

tage that should not be overlooked. The use of electrolytic pumping of oxygen in the electric ROC would permit it to operate at a much lower temperature. Palladium and platinum thus become attractive candidate materials for hydrogen separating membranes. Such a device, operating at 1400K and 30 atm, for example, might easily be expected to produce a "residue" containing mole fractions of 0.9, 0.1, and $\approx 10^{-11}$ water, hydrogen, and oxygen, respectively, from which the hydrogen might be separated by a palladium membrane. Such a device could be made to require no water recirculation, in contrast with a more conventional electrolytic device. Heat exchanger losses would be substantially reduced.

Finally, it is appropriate that we mention a ROC variation, shown in figure 7, which might be used in combination with elec-

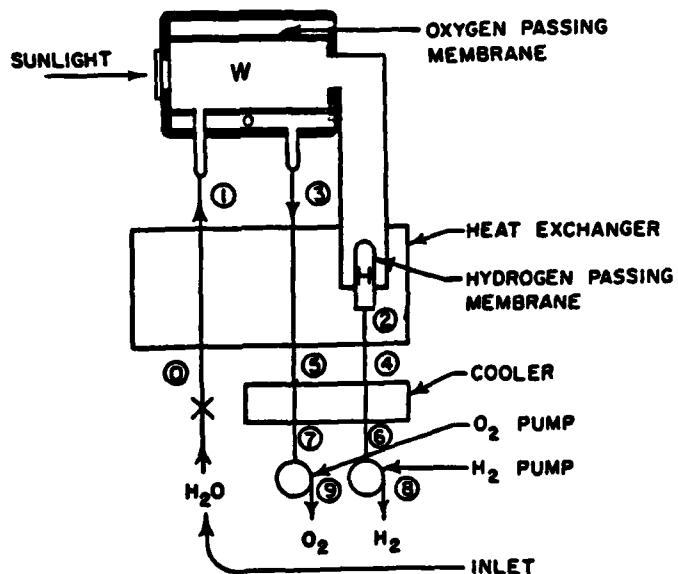


Figure 7. The ROC, modified to permit the use of low-temperature metallic membranes for the diffusion of hydrogen.

trolysis cells or by itself. It is based on an idea first suggested by Ford¹⁰. It may ameliorate the hydrogen membrane material problem. It differs from the ROC only in that its hydrogen passing membrane operates within the heat exchanger at a temperature that is substantially lower than that of the main chamber. In all of its other attributes, it is the same as the ROC. We have not yet evaluated the thermodynamic performance of this modification, however.

VI. CONCLUSION

ROCs are intrinsically thermodynamically capable of greater thermal efficiencies than electric ROCs, and can, ultimately, probably be made to function at higher temperatures. They may be easier to fabricate, because high temperature electrode attachments will not be needed. Electric ROCs offer the tantalizing advantages of permitting us to operate at lower temperatures, where we have more experience with hydrogen diffusion membranes.

It is evident that a great deal of research, analytical as well as experimental, should be done on these interesting systems.

VII. ACKNOWLEDGEMENT

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